

DTIC FILE COPY

(4)

OFFICE OF NAVAL RESEARCH

CONTRACT NO. N00014-86-K-0772

TECHNICAL REPORT NO. 19

AD-A198 857

Molecular Design of Novel Discogen  
Possessing A Semi-Flexible Aryloxytriazine Core

by

J. A. Feldman, J. F. Johnson, and S. J. Huang

Liquid Crystalline Polymer Research Center  
University of Connecticut  
Storrs, CT 06268

Prepared for Publication

in

Molecular Crystals and Liquid Crystals

September 15, 1988

REPRODUCTION IN WHOLE OR IN PART IS PERMITTED FOR ANY  
PURPOSE OF THE UNITED STATES GOVERNMENT.

THIS DOCUMENT HAS BEEN APPROVED FOR PUBLIC RELEASE  
AND SALE; ITS DISTRIBUTION IS UNLIMITED.

DTIC  
ELECTE  
SEP 19 1988  
S E D

88 9 19

# REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION <b>Unclassified</b>			1b RESTRICTIVE MARKINGS <b>None</b>		
2a SECURITY CLASSIFICATION AUTHORITY			3 DISTRIBUTION/AVAILABILITY OF REPORT <b>Approved for Public Release, Distribution Unlimited</b>		
2b DECLASSIFICATION/DOWNGRADING SCHEDULE					
4 PERFORMING ORGANIZATION REPORT NUMBER(S) <b>Technical Report No. 19</b>			5. MONITORING ORGANIZATION REPORT NUMBER(S)		
6a. NAME OF PERFORMING ORGANIZATION <b>University of Connecticut</b>		6b. OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION <b>Office of Naval Research</b>		
6c. ADDRESS (City, State, and ZIP Code) <b>Storrs, CT 06268</b>		7b ADDRESS (City, State, and ZIP Code) <b>800 North Quincy Avenue Arlington, VA 22217</b>			
8a. NAME OF FUNDING/SPONSORING ORGANIZATION		8b OFFICE SYMBOL (If applicable) <b>ONR /DARPA</b>	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER <b>N00014-86-K-0772</b>		
8c. ADDRESS (City, State, and ZIP Code) <b>800 North Quincy Avenue Arlington, VA 22217</b>		10 SOURCE OF FUNDING NUMBERS			
		PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
11 TITLE (Include Security Classification) <b>Molecular Design of Novel Discogen Possessing a Semi-Flexible Aryloxytrianine Core. (Unclassified)</b>					
12 PERSONAL AUTHOR(S) <b>J. A. Feldman, J. F. Johnson, and S. J. Huang</b>					
13a TYPE OF REPORT <b>Technical, Interim</b>		13b TIME COVERED <b>FROM TO 09/15/8</b>		14 DATE OF REPORT (Year, Month, Day) <b>1988-09-15</b>	
				15 PAGE COUNT <b>15</b>	
15 SUPPLEMENTARY NOTATION <b>Submitted to Mol. Cryst. Liq. Cryst. (LCPRC Publication No. LCPRC88)</b>					
17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)		
FIELD	GROUP	SUB-GROUP			
			<b>Discotic Liquid Crystalline Polymers, Aryloxytriazine, triazines. (orig) ←</b>		
19 ABSTRACT (Continue on reverse if necessary and identify by block number) <p>Two compounds have been synthesized which exhibit a discotic mesophase. The molecule includes a semi-flexible tris(benzylidene oxyniline) triazine core flanked by just one alkyl substituent at the 4' position of each radial ring. An oxygen links the benzylidene aniline groups to the central triazine ring. Calorimetric measurements and polarizing microscopy observations show the existence of discotic mesophases. This appears to be the first example of a semi-flexible core with only minimal alkyl substituents which still produces a discotic liquid crystalline phase.</p>					
20 DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS RPT <input type="checkbox"/> DTIC USERS			21 ABSTRACT SECURITY CLASSIFICATION <b>Unclassified</b>		
22a NAME OF RESPONSIBLE INDIVIDUAL <b>Dr. Kenneth J. Wynne</b>			22b TELEPHONE (Include Area Code) <b>(202) 696-4410</b>		22c. OFFICE SYMBOL <b>ONR</b>

MOLECULAR DESIGN OF NOVEL DISCOGEN  
POSSESSING A SEMI-FLEXIBLE ARYLOXYTRIAZINE CORE

J. A. Feldman, J. F. Johnson and S. J. Huang

Institute of Materials Science  
Box U-136  
University of Connecticut  
Storrs, Connecticut 06268

Two compounds have been synthesized which exhibit a discotic mesophase. The molecule includes a semi-flexible tris(benzylidene oxyaniline)triazine core flanked by just one alkyl substituent at the 4' position of each radial ring. An oxygen links the benzylidene aniline groups to the central triazine ring. Calorimetric measurements and polarizing microscopy observations show the existence of discotic mesophases. This appears to be the first example of a semi-flexible core with only minimal alkyl substitutions which still produces a discotic liquid crystalline phase.

Accession For	
NTIS GRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special
A-1	



## Introduction

In 1977 the first discotic mesophase was recognized by Chandrasekhar (1,2). It was a hexa-substituted benzene exhibiting a columnar phase deduced from birefringence studies and x-ray work (3,4). Since this time several other examples of discotic liquid crystals have been reported. The molecular geometry needed to obtain this phase has subsequently fallen into two categories. In each case the main desire is to produce a large surface area to thickness ratio which would enhance the probability of obtaining a discotic mesophase. The two categories can be generally broken down into compounds having a large aromatic core with a high number of flexible substituents, such as those derived from triphenylene (5,6), rufigallol (7,8,9) or truxenes (10), or transition metal complexes, such as bis(dithiolene) nickel (11) or bis(beta-diketonato) copper II (12). The latter approach takes advantage of rigid organic compounds which can bind at two sites with the metal. In all cases the objective is to maximize the surface area with both a large rigid core and as many flexible substitutions as possible.

Recently a discotic liquid crystal has been reported by Lattermann having a less rigid core but maintaining a high degree of flexible substitutions (13). The core consisted of 1,3,5-tris(benzoyloxy)benzene. There are a total of nine flexible decyloxy groups bonded, three to each benzoyloxy ring. The total molecule was shown to possess a relatively large surface area when the flexible arms were in the all trans conformation. Intuitively it seems that the core of the molecule would play a greater role in enhancing the discotic behavior than the alkyl or alkoxy substituents. For this reason it was decided to synthesize a molecule having a larger core at the expense of the high number of flexible arms and further a flexible core relative

to examples cited above. The molecular design included here suggests that the discotic phase may be favored due to specific packing requirements even though there would be much empty space within the disc as a result of the flexible central oxygen links and the lack of a multitude of aliphatic substituents. The compounds synthesized were 1,3,5-tris(4-benzylidene oxy-4'-R-aniline)triazines, where R is either hexyl or decyl.

### Experimental

All reagents were received from Aldrich Chemical and purified before use. To a 100 ml RBF equipped with magnetic stirrer and condenser was added 50 ml EtOH and 1.1 equivalents of 4-hydroxybenzaldehyde. Next one equivalent of the alkyl aniline was added and a catalytic amount of p-TsOH. This was stirred and refluxed for 4 hours. Upon cooling the product precipitated from solution. The yellow solid was collected by vacuum filtration, washed with cold EtOH then recrystallized with EtOH. The 4-hydroxybenzylidene-4'-alkyl aniline was then reacted with cyanuric chloride.

To a 50 ml RBF equipped with magnetic stirrer and argon purge was added 25 ml dry EtOH followed by 4 equivalents of the 4-hydroxybenzylidene-4'-alkyl aniline and 4 equivalents of sodium hydroxide. Once the solution cleared one equivalent of cyanuric chloride was added and the solution was stirred at room temperature for 6 hours. The sodium chloride was filtered off and upon neutralization of the solution the product precipitated out. The product was filtered, washed with distilled water, EtOH and ether to remove the remaining starting materials. The product was then recrystallized from acetone producing pale yellow crystals. The purity was checked with thin layer chromatography using tetrahydrofuran and then chloroform as mobile phases.

The thermal properties were evaluated using a Perkin-Elmer DSC-7 at heating and cooling rates of 2°C/min. The onset of each transition is provided, the melting points are uncorrected. The optical properties were

examined using a Nikon Labophot under crossed-polars, magnifications are included with each photograph. A Linkam Scientific TH-600 Hot Stage along with a TMS 90 Controller were used at rates ranging from 5°C/min to 0.5°C/min. The exact rate is included with the photograph.

### Results and Discussion

The thermal and optical properties will be assessed for each compound separately. The first compound, hexyl substituent, exhibited three transitions on the first heating as shown in Figure 1. A crystal to crystal transition occurred at 125.0°C having a molar enthalpy of 6.13 kJ/mole. This was followed by a sharp melting point at 153.8°C having an enthalpy of 26.1 kJ/mole. This peak coincides with an optical transition from a sky blue crystalline phase to a yellow mesophase. The material was fluid at this stage. The transition from the discotic phase to isotropic phase occurred at 197.5°C and  $\Delta H=6.50$  kJ/mole, corresponding to the loss of all birefringence under the microscope. This compound was thermally well behaved in that the liquid crystalline transitions were readily reversible. Upon cooling the discotic phase was reentered at 199.5°C corresponding to the nucleation of liquid crystalline domains. These domains shown in Figure 3 exhibited classic discotic texture of the columnar phase being very similar to textures reported (5,7,14). The crystalline phase was reentered at 141.5°C. At this point the sky blue texture of the solid phase reappeared as well as a complete textural reorganization. The crystal to crystal transition was not observed while cooling and did not show up on subsequent thermal scans. Upon second heating and cooling the crystal to discotic transition and the discotic to isotropic transition were again observed at temperatures within 0.5°C of the first scan. This thermogram is presented in Figure 4. The thermal properties for this compound were reversible and reproducible.

The second compound was synthesized using 4-decyylaniline. The difference in the number of carbons around the perimeter of the disc changed the optical texture which seemed to be due to an increase in viscosity and packing variations. Certain textures could be induced upon shearing which were not observed with the lower molecular weight analog. The first thermal scan is shown in Figure 5. There was no crystal to crystal transition. A crystal to discotic transition was observed at 75.5°C. The molar enthalpy of this transition was 45.2 kJ/mole. This melting point was observed under the microscope but at a slightly different temperature due to sample preparation. The material did not readily flow so that sample was sheared in order to assure its fluid nature and to improve the optical transmittance, the texture is shown in Figure 6. The exact nature of this mesophase is being deduced using x-ray diffraction experiments although it resembled textures reported previously (6). The clearing point was reached at 114.0°C having an enthalpy of 60.5 kJ/mole. Upon cooling the mesophase was obtained as before. This is exemplified by the cooling scan seen in Figure 5 where the discotic phase was reached at 103.5°C, the enthalpy equalling -20.2 kJ/mole. There were multiple peaks observed which may be due to molecular reorganization or slight amounts of impurities. The discotic to crystal transition was bimodal beginning at 81.0°C,  $\Delta H = -9.45$  kJ/mole. The second thermal scan of this sample is shown in Figure 7. Here the melting transitions became much broader with the crystal to discotic transition occurring at 74.7°C and the discotic to isotropic transition occurring at 100.1°C. Upon cooling, the sample entered the discotic phase at 100.6°C and interestingly there was only one peak. The bimodal discotic to crystal transition remained with the first transition beginning at 86.4°C and second transition beginning at 82.8°C. This may indicate the existence of another mesophase which will be assessed in the future.

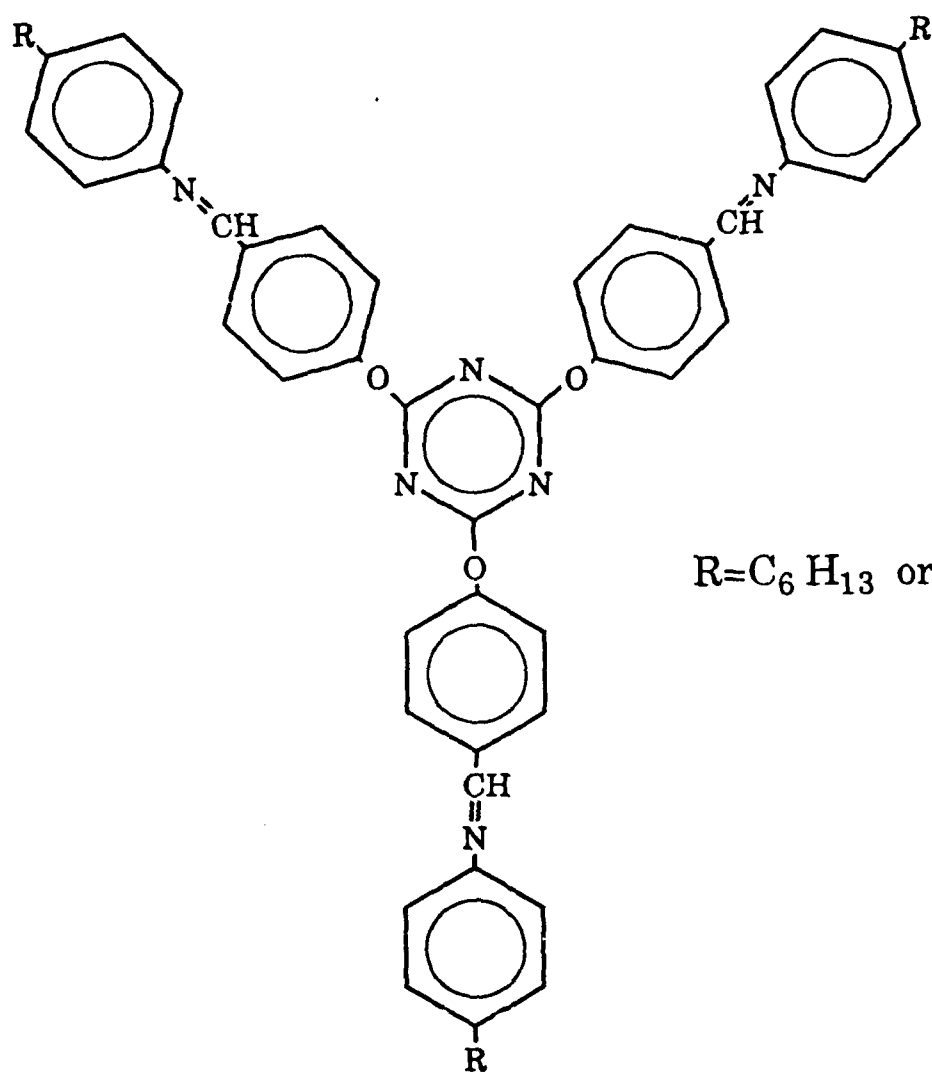
### Concluding Remarks

In this study it was found that discotic liquid crystalline phases are exhibited for compounds having a relatively flexible core and only three alkyl substituents. This opens new questions as to the validity of the hypothesis that a rigid core with maximum number of alkyl or alkoxy substituents is needed to form such a phase. Further investigations are being undertaken to include the analogs between these two. In this way complete x-ray measurements and spectroscopic studies can be performed and reported. Phase diagrams will be developed to better understand this new set of discotic liquid crystals.



## Bibliography

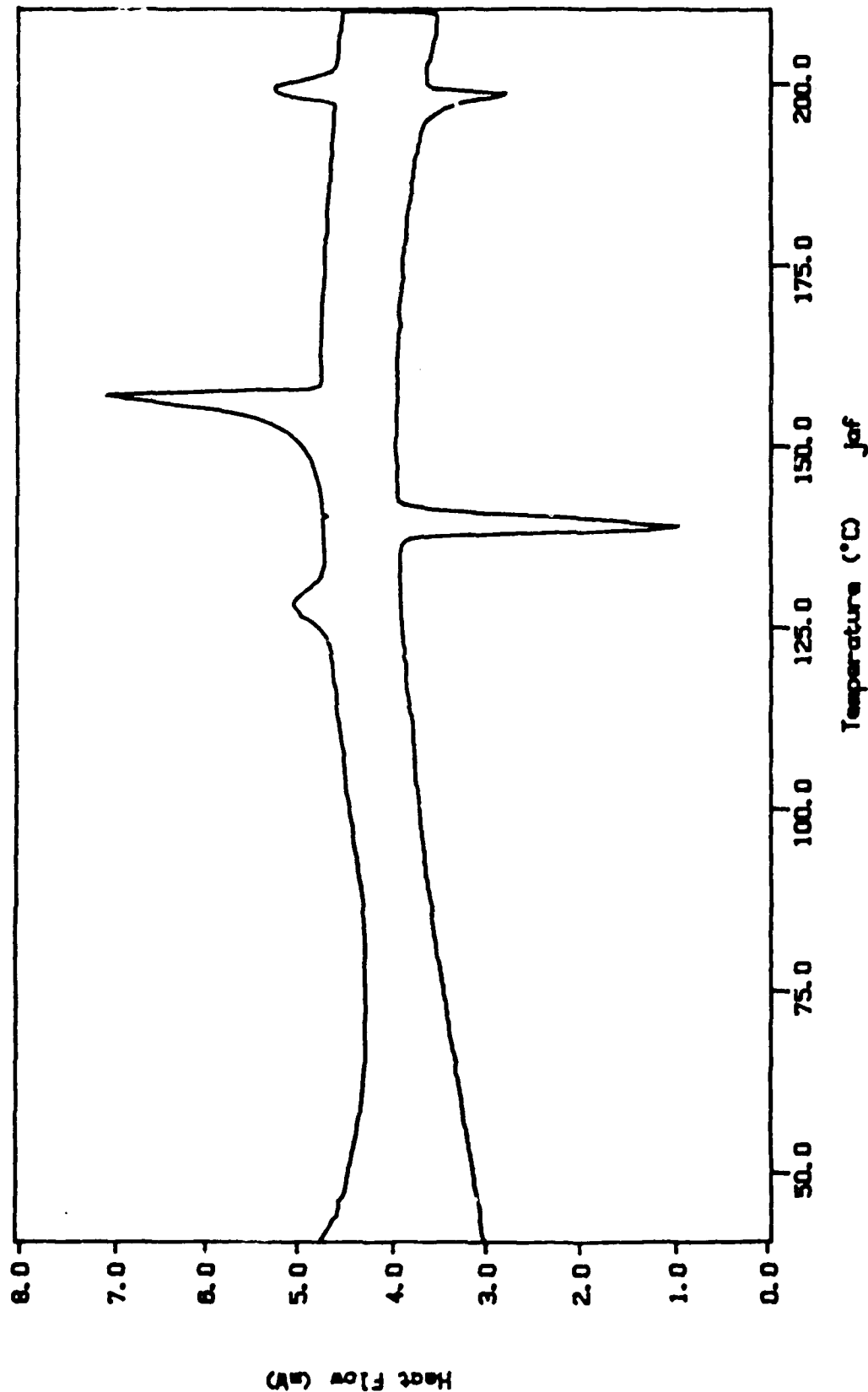
1. S. Chandrasekhar, Indian J. of Pure and Appl. Phys., 19, 769, 1981.
2. S. Chandrasekhar, Mol. Cryst. Liq. Cryst., 63, 171, 1981.
3. A. M. Levelut, J. de Physique Orsay, 47(2), 351, 1986.
4. A. M. Levelut, J. de Physique Lett., 40, L-81, 1979.
5. C. Destrade, M. C. Mondon-Bernaud and N. H. Tinh, Mol. Cryst. Liq. Cryst., 169, 49, 1979.
6. C. Destrade, M. C. Bernaud, H. Gasparoux, A. M. Levelut and N. H. Tinh, Liquid Crystals-Proc. Intl. Conf.-Bangalore, ed. S. Chandrasekhar, 29, Heyden Publ., London, 1989.
7. A. Queninger, A. Zann, J. C. Dubois and J. Billard, Liquid Crystals-Proc. Intl. Conf.-Bangalore, ed. S. Chandrasekhar, 35, Heyden Publ., London, 1979.
8. C. Cartagna, A. Roviello and A. Sirigu, Liquid Crystals, 2(5), 611, 1987.
9. C. Cartagna, A. Roviello and A. Sirigu, Mol. Cryst. Liq. Cryst., 122, 151, 1985.
10. N. H. Tinh, R. Cayuela, C. Destrade, Mol. Cryst. Liq. Cryst., 122, 141, 1985.
11. K. Ohta, A. Takagi, H. Muroki, I. Yamamoto, K. Matsuzaki, T. Inabe and Y. Maruyama, Mol. Cryst. Liq. Cryst., 147, 15, 1987.
12. K. Ohta, A. Takagi, H. Muroki, I. Yamamoto, and K. Matsuzaki, Mol. Cryst. Liq. Cryst., 147, 61, 1987.
13. G. Lattermann, Liquid Crystals, 2(5), 723, 1987.
14. N. H. Tinh, P. Foucher, C. Destrade, Mol. Cryst. Liq. Cryst., 111, 277, 1984.



DSC Data File: cdt1  
 Sample Weight: 7.400 mg  
 Tue Feb 24 05:19:32 1987  
 CB-tria

PERKIN-ELMER

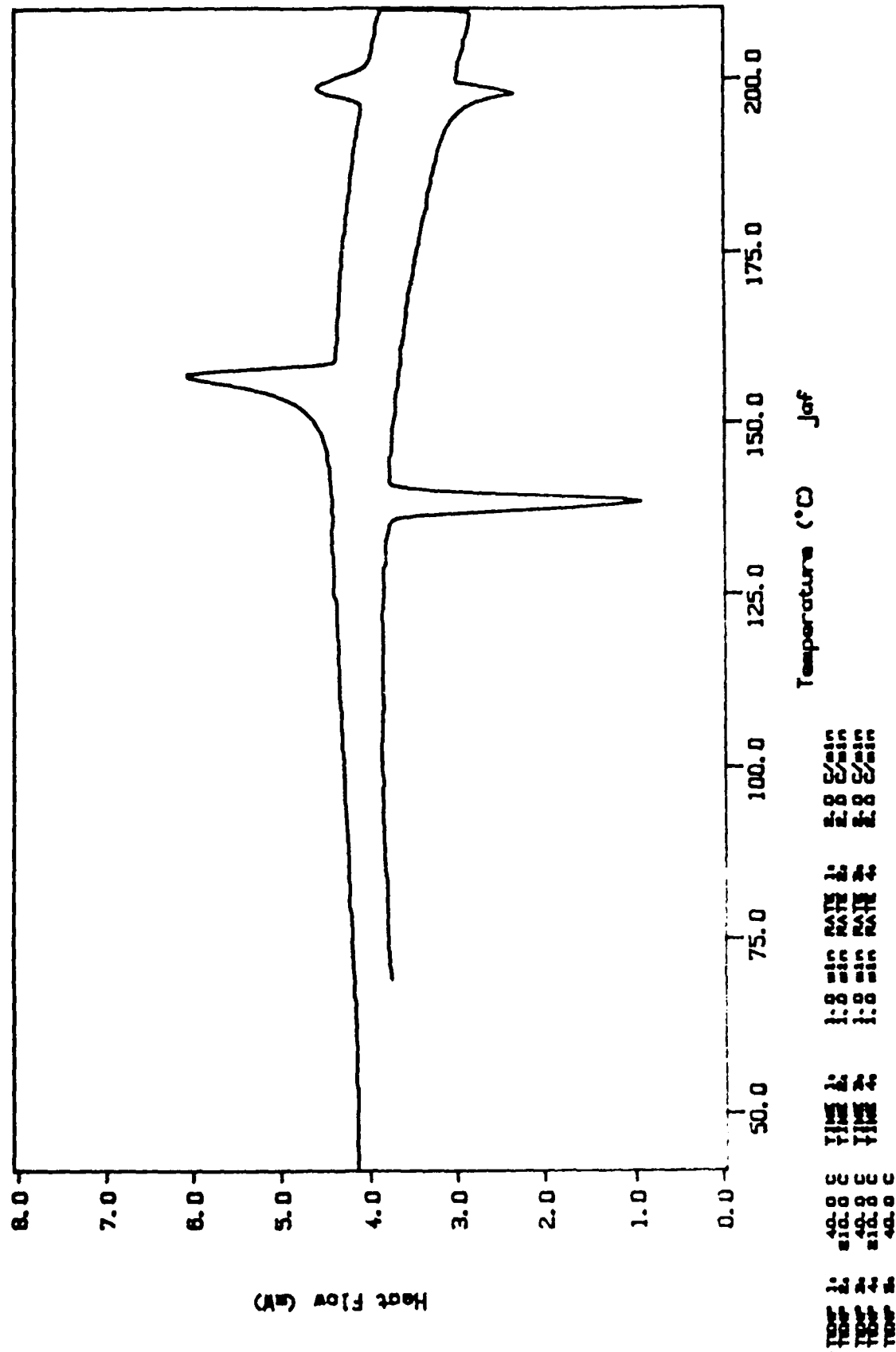
7 Series Thermal Analysis System



18.8 g 11.8 g 11.8 g 11.8 g  
 18.8 g 11.8 g 11.8 g 11.8 g  
 40.0 g

DSC Data File: 08t2h  
 Sample Weight: 7.400 mg  
 Tue Feb 24 08:00:17 1987  
 08-t2h1a 2nd htg

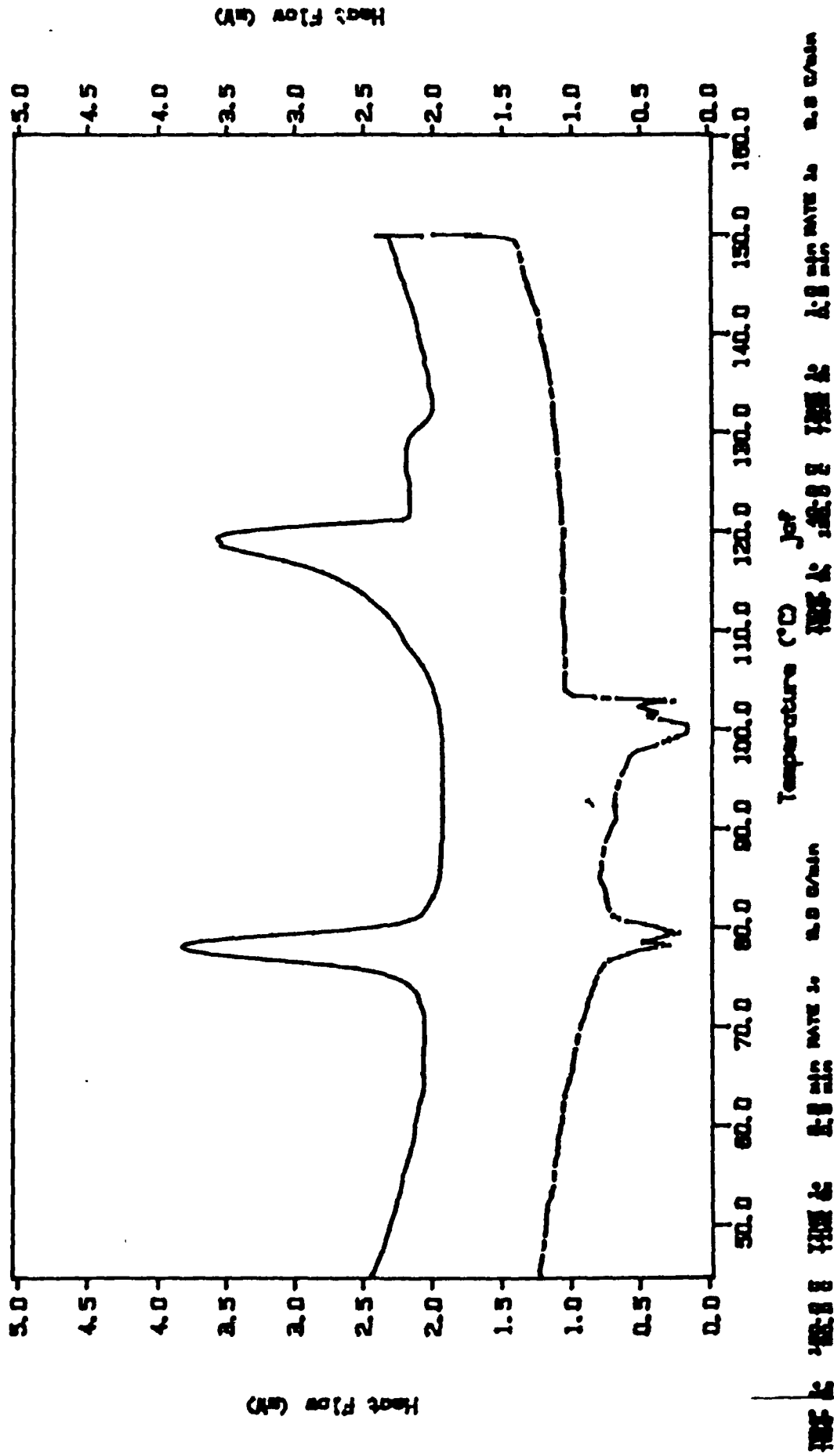
# PERKIN-ELMER 7 Series Thermal Analysis System



DSC Data File: el0tr  
Sample Weight: 4.600 mg  
Tue Feb 24 08:11:00 1987  
el0tr1etria

PERKIN-ELMER  
7 Series Thermal Analysis System

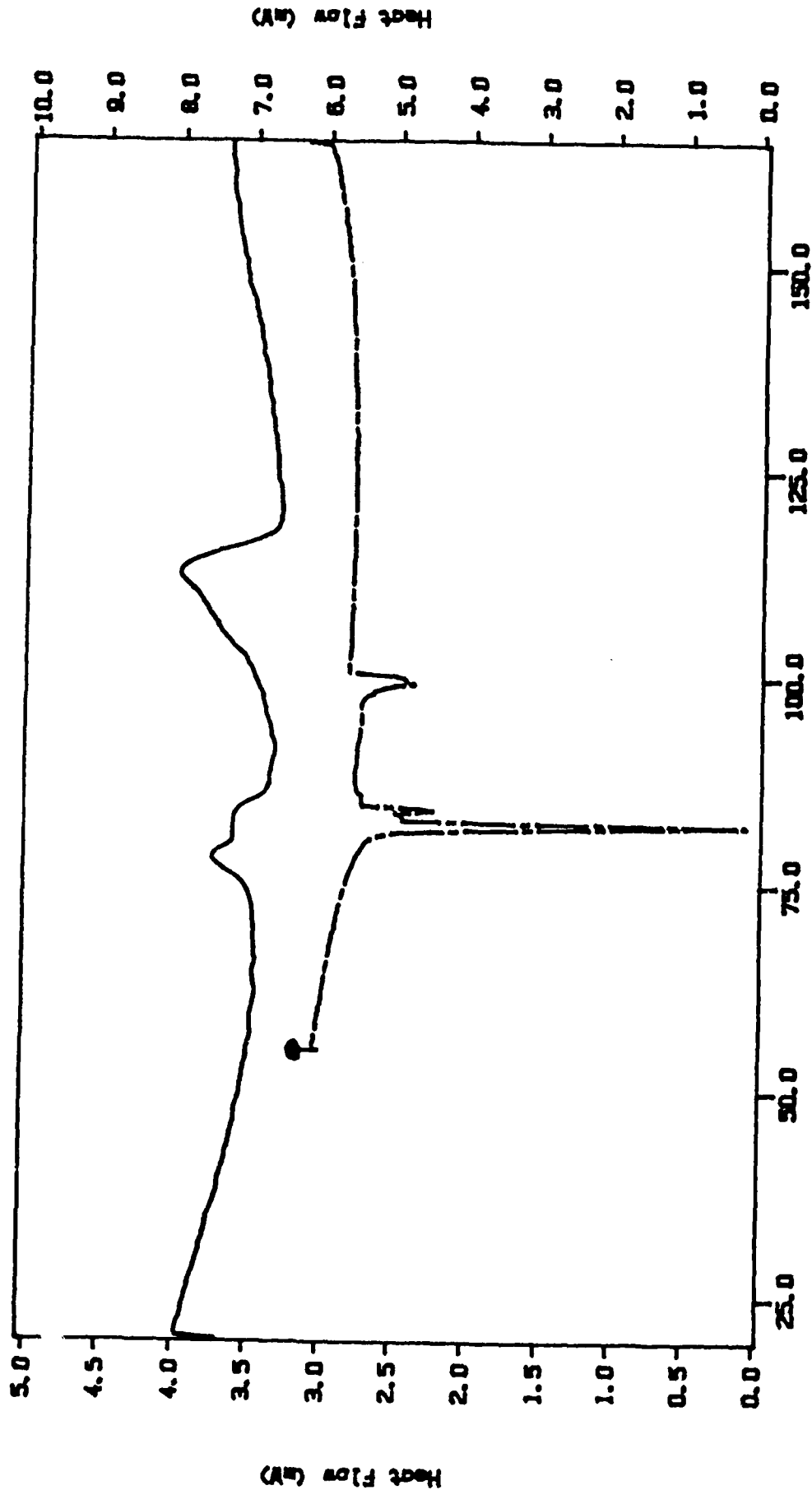
DSC Data File: el0tr  
Sample Weight: 4.600 mg  
Tue Feb 24 08:11:00 1987  
el0tr1etria



DSC Data File: c10tr  
Sample Weight: 4.800 mg  
Time: Feb 24 08:11:00 1987  
c10tr-1e-1a

PERKIN-ELMER  
7 Series Thermal Analysis System

DSC Data File: c10tr  
Sample Weight: 4.800 mg  
Time: Feb 24 08:11:00 1987  
c10tr-1e-1a



TEMP: 1: 100.0°C TIME: 1: 0.0 min RATE: 1: 0.0 °C/min  
TEMP: 2: 100.0°C TIME: 2: 0.0 min RATE: 2: 0.0 °C/min

TECHNICAL REPORT DISTRIBUTION LIST, GEN

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Attn: Code 1113 800 N. Quincy Street Arlington, Virginia 22217-5000	2	Dr. David Young Code 334 NORDA NSTL, Mississippi 39529	1
Dr. Bernard Douda Naval Weapons Support Center Code SOC Crane, Indiana 47522-5050	1	Naval Weapons Center Attn: Dr. Ron Atkins Chemistry Division China Lake, California 93555	1
Naval Civil Engineering Laboratory Attn: Dr. R. W. Drisko, Code LS2 Port Hueneme, California 93401	1	Scientific Advisor Commandant of the Marine Corps Code RD-1 Washington, D.C. 20380	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	12 high quality	U.S. Army Research Office Attn: CRD-AA-IP P.O. Box 12211 Research Triangle Park, NC 27709	1
DTNSRDC Attn: Dr. H. Singerman Applied Chemistry Division Annapolis, Maryland 21401	1	Mr. John Boyle Materials Branch Naval Ship Engineering Center Philadelphia, Pennsylvania 19112	1
Dr. William Tolles Superintendent Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1	Naval Ocean Systems Center Attn: Dr. S. Yamamoto Marine Sciences Division San Diego, California 91232	1

END

DATE

FILMED

DTIC

11-88